

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {.....}

EPA MRID Number 46258601

Data Requirement: PMRA Data Code:
EPA DP Barcode: D303152
OECD Data Point:
EPA Guideline: 162-3



Test material: [3,4-¹⁴C]Glufosinate ammonium. **Purity:** 96.0%
Common name: Glufosinate ammonium.
Chemical name
IUPAC: Ammonium DL-homoalanin-4-yl(methyl)-phosphinate.
CAS name: 2-Amino-4-(hydroxymethylphosphinyl)butanoic acid, ammonium salt.
CAS No: 77182-82-2.
Synonyms: Basta, AE F039866, HOE 039866.
SMILES string: CP(=O)(CCC(C(=O)O)N)[O-][N+].

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Date: 4-27-06

Company Code:
Active Code:
Use Site Category:
EPA PC Code: 128850

Date Evaluation Completed: Apr. 27, 2006

CITATION: Stupp, H. 2003. Degradation and Metabolism of Glufosinate Ammonium in Soil under Anaerobic Conditions. Study ID: M1261285-5. Unpublished study performed and submitted by Bayer CropScience, Monheim, Germany. December 16, 2003. 62 pp.



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EXECUTIVE SUMMARY:

The biotransformation of [3,4-¹⁴C]ammonium DL-homoalanin-4-yl(methyl)-phosphinate (glufosinate ammonium) was studied in water/sandy loam soil (deionized water; soil pH 6.0, organic matter 1.6%) from Germany for 125 days under anaerobic conditions in darkness at 20 ± 1 °C. [¹⁴C]Glufosinate ammonium was applied at a rate of 1.63 mg a.i./L (1.96 mg a.i./kg soil), which was estimated to be equivalent to approximately 1.5 kg a.i./ha soil. The soil:water ratio was approximately 1:1.2 (100 g:120 mL); the soil was flooded to a depth of 1-2 cm. This experiment was conducted in accordance with EC and SETAC guidelines and in compliance with OECD-GLP standards, which may differ from those of FIFRA. The test system consisted of sealed biometer flasks (300 mL) containing treated flooded soil maintained under an argon atmosphere. At the time of sampling, the samples were purged so that exiting gases passed through a soda lime trap, an oxidizer (muffle furnace, CuO), and scintillation fluid. Duplicate flasks were collected at 0, 1, 5, 7, 13, 29, 63, 95 and 125 days posttreatment. The samples were centrifuged, and the water layer was decanted. Soil samples were sequentially extracted by shaking three times with water at ambient temperatures, by stirring once with water at 60-70 °C, and by shaking once with acetonitrile:water (1:1, v:v) at ambient temperatures. The aqueous phase and soil extracts were not analyzed separately. The floodwater and the soil extracts using ambient water were combined (CE), and the hot water and acetonitrile:water extracts were combined separately (HE). Combined extracts CE and HE were analyzed for total radioactivity using LSC and for specific [¹⁴C]compounds using HPLC. [¹⁴C]Compounds were identified by comparison to reference standards of glufosinate hydrochloride, 3-methylphosphinico-propionic acid, 2-methylphosphinico-acetic acid, and disodium L-2-acetamido-4-methylphosphinobutyrates. The volatile traps and extracted soil were analyzed using LSC or LSC following combustion.

Anaerobicity in the test system was not achieved and maintained, as conditions in the test system were moderately reducing to reducing throughout the study. Redox potentials of the water layer ranged from -71 mV to -30 mV; redox potentials in the soil layer were not determined. The pH ranged from 4.51 to 5.3. Daily temperatures averaged *ca.* 20.3 °C.

Overall recoveries of radiolabeled material averaged 97.3 ± 1.4% (range 94.3-99.5%) of the applied, with no decline in material balances. Since the water and soil layers were not analyzed separately, the ratio of residues in the water to the soil could not be determined. The ratio of extractable residues to soil bound residues was *ca.* 19:1 immediately posttreatment, 9:1 at 7 days, and 4:1 at 125 days.

In the total system, [¹⁴C]glufosinate ammonium decreased from an average 88.6% of the applied at 0 days posttreatment to 80.8% at 13 days, then varied between 70.3 to 72.7% at 29 through 125 days. No major or minor transformation products were isolated. Two unidentified minor impurities were identified in the application solution and throughout the study, both at ≤3.2% of the applied. Almost all extractable residues were identified as glufosinate ammonium at each sampling interval. The concentration of extractable [¹⁴C]residues in the soil decreased from an average 94.4% of the

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applied at 0 days posttreatment to 75.1-77.0% of the applied at 63-125 days, and nonextractable [¹⁴C]residues increased to a maximum average of 21.0-21.5% at 63-125 days. At 125 days posttreatment, volatilized [¹⁴C]residues totaled <0.2% of the applied. Using data for individual samples, glufosinate ammonium dissipated in the entire system with a log-linear half-life of 415 days. This half-life is of uncertain value because it is extrapolated well beyond the duration of the study. Glufosinate ammonium was stable to anaerobic aquatic metabolism in this study, as no degradates were produced.

A transformation pathway was proposed by the study author. Glufosinate ammonium dissipates as a result of binding to the soil.

Results Synopsis:

Test system used: water-sandy loam soil.

Half-lives:

Water:	Concentrations in the water layer were not determined.
Soil:	Concentrations in the soil layer were not determined.
Entire system dissipation:	415 days (log-linear, $r^2 = 0.6398$).

Entire system degradation: Stable.

Major transformation products: None.

Minor transformation products: None.

Study Acceptability: This study is classified as **supplemental**. It does not meet requirements for an anaerobic aquatic metabolism study because the sediment and water phases were not analyzed separately and sufficient anaerobicity (-100 mV) was not achieved and maintained. Furthermore, the experiment was conducted using soil and deionized water rather than an anaerobic sediment and natural water.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was conducted in accordance with SETAC- Europe Procedures for Assessing the Environmental Fate and Ecotoxicology of Pesticides (1995), European Economic Community Commission Directive 95/36/EC, OECD Guideline 307 (pp. 1, 13). The following significant deviations from OECD Guideline 308 were noted:

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The sediment and aqueous phases were not collected from the anaerobic zones of surface water bodies, and only one system was studied.

Sufficiently reducing conditions (-100 mV) were not achieved and maintained throughout the study.

The sediment and water phases were not analyzed separately.

COMPLIANCE:

This study was conducted in compliance with OECD Good Laboratory Practice standards, which may differ from those of FIFRA (p. 3). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Certification of Authenticity statements were provided (pp. 2-5).

A. MATERIALS:

1. Test Material:

[3,4-¹⁴C]Glufosinate ammonium converted from [3,4-¹⁴C]glufosinate hydrochloride (pp. 14-15).

Chemical Structure:

See DER Attachment 1.

Description:

Solid (p. 15).

Purity:

Radiochemical purity: 97.3% (glufosinate hydrochloride).
Batch No.: X33007 (glufosinate hydrochloride).
Analytical purity: 96.0% (glufosinate ammonium).
Specific activity: 6.349 MBq/mg (glufosinate hydrochloride).
Location of radiolabel: Labeled on the 3 and 4 carbons (p. 15, Figure 1, p. 38).

Storage conditions of test chemical:

The test substance was stored at -20°C, and reference compounds were stored refrigerated (p. 16).

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Table 1: Physico-chemical properties of glufosinate ammonium.¹

Parameter	Values	Comments
Molecular weight:	198.2 g/Mol.	
Molecular formula:	C ₅ H ₁₅ N ₂ O ₄ P	
Water solubility:	>500 g/L	At 20°C.
Vapor pressure:	<3.1 x 10 ⁻⁵ Pa	At 50°C.
UV absorption:	Not reported.	
pK _a :	9.15	Ammonium salt
K _{ow} /log K _{ow} :	Not reported.	
Stability of compound at room temperature:	Not reported.	

1. Data obtained from pp. 14-15 of the study report.

2. Water-soil collection, storage and properties:

Table 2: Description of water-soil collection and storage.¹

Description		Details
Geographic location:		Soil was obtained from Frankfurt-Hoechst, Germany, 50°06' N. latitude, 8°32' longitude East Greenwich. Deionized water (Milli-Q) was used in the study.
Collection date:		March 4, 2003.
Pesticide use history at the collection site:		No pesticide use known; the site was not agricultural.
Collection procedures:	Water:	Not applicable.
	Soil:	Sampled with a shovel and placed into plastic bags.
Sampling depth:	Water:	Not applicable.
	Soil:	Top 20 cm (8").
Storage conditions:		Soil was stored in plastic bags at <i>ca.</i> 7°C.
Storage length:		Approximately 2 months (from March 3 to April 28, 2003).
Preparation:	Water:	Deionized water was used.
	Soil:	Air-dried and sieved (≤ 2.0 mm). The soil was flooded, treated with saccharose, and pre-incubated under a nitrogen atmosphere for <i>ca.</i> 36 days prior to treatment.

1. Data obtained from pp. 16-17, Appendix 2, p. 56 of the study report.

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Table 3: Properties of the water.¹

Property	Details
Temperature (°C):	Not reported.
pH:	Not reported.
Redox potential:	Not reported.
Oxygen concentration:	Not reported.
Dissolved organic carbon (DOC):	Not reported.
Total organic carbon (TOC):	Not reported.
Hardness:	Not reported.
Electrical conductivity (μ mhos):	Not reported.
Biomass (mg microbial C/100 g or CFU or other):	Not reported.

1. Deionized water was used in the study (p. 12).

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Table 4: Properties of the soil.¹

Property	Details
Textural classification:	Sandy loam.
% Sand (2000 - 50 μ M):	56.4
% Silt (<50-2 μ M):	31.4
% Clay (<2 μ M):	12.2
pH (in 10 mM CaCl ₂):	6.0
Organic carbon (%) ² :	0.9
Organic matter (%):	1.6
CEC (meq/100 g soil):	6.2
Redox potential:	Not reported.
Maximum Water Holding Capacity (%)	35.9
% Moisture at 1/3 bar:	19.9
Bulk density (disturbed, g/cm ³):	1.2
Biomass (mg C/kg) ³ :	235/212
Taxonomic classification:	Not reported.
Other:	Not reported.

1. Data obtained from Table 1, p. 32 of the study report.

2. Calculated by the study author using the equation % OM = % OC x 1.724.

3. Biomass at 0 days before flooding.

B. EXPERIMENTAL CONDITIONS:

1. Preliminary experiments: No preliminary experiments were reported.

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2. Experimental conditions:

Table 5: Study design.¹

Parameter		Details
Duration of the test:		125 days.
Water:		
Filtered/unfiltered water:		Deionized water.
Type and size of filter used, if any:		Not applicable.
Amount of soil and water per treatment:	Water:	120 mL, so that the soil was flooded to a depth of 1-2 cm.
	Soil:	100 g (dry wt. equivalent).
Water/soil ratio:		1.2:1 (120 mL water:100 g soil).
Nominal application rate (mg a.i./L):		1.67 (equivalent to 2 mg a.i./kg soil, calculated from 1.5 kg a.i./ha assuming a soil depth of 5 cm and a bulk density of 1.5 g/cm ³).
Measured application rate (mg a.i./L):		1.63 (equivalent to 1.96 mg a.i./kg soil).
Control conditions, if used:		No sterile controls were used.
No. of Replications:	Controls, if used:	No sterile controls were used.
	Treatments:	Duplicate flasks were collected at each sampling interval.
Test apparatus (Type/material/volume):		Biometer-type flasks (300 mL) containing treated flooded soil (120 mL water, 100 g soil) were flushed with argon and sealed with caps containing two inlet/outlet ports. One port consisted of a purge valve that was closed during incubation. The second port was covered with an argon-flushed balloon. The samples were incubated in a dark climatic cabinet that had been flushed with nitrogen. The test apparatus is illustrated in Figure 3, p. 41.
Details of traps for CO ₂ and organic volatiles, if any:		At the time of sampling, each replicate flask was attached to a volatile trapping system that drew the headspace of the flask and the balloon through a trap with soda lime, an oxidizer (muffle furnace, tube with CuO), and three tubes of scintillation cocktail. The volatile trapping system is illustrated in Figure 4, p. 42.
If no traps were used, is the system closed/open?		A volatile trapping system was used.
Identity and concentration of co-solvent:		None; the test substance was dissolved in water.

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Test material application:	Volume of test solution used/treatment:	235 μ L/sample.
	Application method:	The stock solution was applied homogeneously to the water surface.
Any indication of the test material adsorbing to the walls of the test apparatus?		None.
Biomass of controls:		Controls were not used.
Biomass of treated soil:	Initial (0 Days pre flood)	235/212 mg microbial C/kg soil (dry wt).
	Final (125 days)	183/248 colonies of anaerobic bacteria/mL, with 10E-04 dilution (1 g soil per 10 mL solution).
Experimental conditions:	Temperature ($^{\circ}$ C):	20.3 \pm 1 $^{\circ}$ C
	Continuous darkness:	Yes.
Other details, if any:		None.

1. Data obtained from pp. 12, 14, 16, 17, 19; Tables 1-2, pp. 32-33; Appendix 3, p. 57 of the study report.

3. Aerobic/Anaerobic conditions: Samples were purged with argon following dosing, sealed, and kept in a nitrogen-filled box during the study (pp. 18-19). Redox potentials in the water layer were -30/-42 mV in duplicate samples at the time of treatment and ranged from -71 mV to -30 mV throughout the study (moderately reducing to reducing; Appendix 4, p. 58). Redox potentials in the soil layer were not reported.

4. Supplementary experiments: No supplementary experiments were reported.

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5. Sampling:

Table 6: Sampling details.¹

Criteria	Details
Sampling intervals:	0, 1, 5, 7, 13, 29, 63, 95 and 125 days.
Sampling method:	Duplicate flasks were collected at each interval.
Method of collection of CO ₂ and volatile organic compounds:	The flasks were purged at each sampling interval, and exiting gases were passed through a volatile trapping system.
Sampling intervals/times for: Sterility check, if sterile controls are used:	Sterile controls were not used.
Redox potential/dissolved oxygen/pH of water layer and redox potential of soil:	The redox potential and pH of the water layer were measured at each sampling interval. The redox potential of the soil was not measured.
Sample storage before analysis:	Samples were extracted on the day of collection. The extracts were analyzed by LSC and HPLC within a few days. Volatile traps, other than the soda lime, were analyzed directly after sampling. Soda lime traps were stored at <-20°C and analyzed within ca. 1 month.
Other observations, if any:	None.

1. Data obtained from p. 20, Table 3, p. 34, Appendix 4, p. 58 of the study report.

C. ANALYTICAL METHODS:

Separation of the soil and water: The water and soil were separated by centrifugation (4,000 rpm, 15 minutes; p. 21; Figure 6, p. 44). The water layer was decanted.

Extraction/clean up/concentration methods: The soil was extracted three times by shaking with water (80 mL) for 30-45 minutes/extraction at ambient temperatures (p. 21, Figure 6, p. 44). After each extraction, the samples were centrifuged and the supernatant decanted. The ambient water extracts were pooled with the water layer and aliquots were analyzed using LSC and HPLC. The soil was then extracted once by stirring with water (120 mL) at 60-70°C for 120 minutes, followed by extraction with acetonitrile:water (1:1, v:v, 120 mL) for 30 minutes at room temperature. After each extraction, the samples were centrifuged and the supernatants decanted; the hot water and acetonitrile:water extractions were pooled and aliquots were analyzed using LSC and HPLC.

Nonextractable residue determination: The extracted soil was air-dried and homogenized in a planetary mill, and portions (0.5-1 g) were analyzed for total radioactivity by LSC following combustion (p. 22).

Volatile residue determination: Organic [¹⁴C]volatiles oxidized by the CuO and trapped in the scintillation cocktail were analyzed using LSC (p. 21). [¹⁴C]Residues trapped in the soda lime,

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presumed to be $^{14}\text{CO}_2$, were liberated using 18% HCl; volatile residues were passed through scintillation cocktails with streams of nitrogen. Scintillation cocktails were analyzed using LSC.

Total ^{14}C measurement: Total [^{14}C]residues were determined by summing the concentrations of residues measured in the water plus soil extracts, the extracted soil, and the volatile traps (Table 4, p. 35).

Derivatization method, if used: A derivatization method was not employed.

Identification and quantification of parent compound: The samples were analyzed using HPLC under the following conditions (p. 23): Spherisorb SAX column (anion exchange; 4.0 mm x 250 mm, 5 μm), an isocratic mobile phase consisting of (A) 5 mM potassium dihydrogen phosphate in pH 2.0 water (adjusted with phosphoric acid) and (B) methanol [A:B, 90:10, v:v]; a flow rate of 1 mL/minute; and radioactive flow detection. Glufosinate ammonium was identified by comparison to an unlabeled reference standard (see below).

The identification of glufosinate ammonium was confirmed using HPLC using an anion exchange column [Nucleosil 100-5 SB (M&N) column (4.0 mm x 250 mm, 5 μm)] eluted with 5 mM disodium sulfate in water for 45 minutes at a flow rate of 1 mL/minute and radioactive flow detection (p. 24).

Identification and quantification of transformation products: Transformation products were separated and quantified by HPLC as described for the parent (p. 23). The reference standards are as follows:

Table 7: Reference standards.¹

Reference standard	Code	Purity	Elution Order
Glufosinate hydrochloride	AE F035125	97.3%	1
3-Methylphosphinico-propionic acid	AE F061517	96.6%	2
2-Methylphosphinico-acetic acid	AE F064619	98.4%	4
Disodium L-2-acetamido-4-methylphosphinato-butyrate	AE F099730	96.7%	3

1. Data obtained from Figure 1, pp. 38, 39 and Figure 9, p. 49.

Detection limits (LOD, LOQ) for the parent compound: The LSC Limit of Detection was twice background (1 Bq) and the HPLC LOD was *ca.* 1% of the applied (pp. 22-24). The Limits of Quantification were not reported.

Detection limits (LOD, LOQ) for transformation products: The LOD and LOQ were the same as described for the parent.

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II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: Conditions in the test system were moderately reducing to reducing throughout the study, with redox potentials ranging from -71 mV to -30 mV (Appendix 4, p. 58). The pH ranged from 4.51 to 5.3. Daily temperatures averaged 20.27°C, with a minimum of 20.00°C and a maximum of 21.30°C (Appendix 3, p. 57).

B. MATERIAL BALANCE: Overall recoveries of radiolabeled material averaged $97.3 \pm 1.4\%$ (range 94.3-99.5%) of the applied, with no decline in material balances (Table 4, p. 35). Since the water layer was not analyzed separately, the ratio of residues in the water and soil could not be determined. The ratio of extractable residues to soil bound residues was *ca.* 19:1 immediately posttreatment, 9:1 at 7 days, and 4:1 at 125 days.

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Table 8: Biotransformation of [^{14}C]glufosinate ammonium, expressed as percentage of applied radioactivity, in water/sandy loam soil under anaerobic conditions (mean \pm SD, n = 2).¹

Compound		Sampling times (days)								
		0	1	5	7	13	29	63	95	125
Glufosinate ammonium	Water ²	Not determined.								
	Soil ²	Not determined.								
	System	88.6 \pm 0.4	87.5 \pm 0.8	86.8 \pm 0.1	81.9 \pm 0.5	80.8 \pm 1	72.5 \pm 0.7	70.3 \pm 1.1	71.0 \pm 0.6	72.7 \pm 0.5
Z1	Water ²	Not determined.								
	Soil ²	Not determined.								
	System	2.6 \pm 0.0	2.2 \pm 0.2	2.3 \pm 0.0	2.4 \pm 0.54	1.7 \pm 0.0	2.3 \pm 0.1	2.6 \pm 0.1	3.0 \pm 0.3	2.6 \pm 0.0
Z2	Water ²	Not determined.								
	Soil ²	Not determined.								
	System	3.2 \pm 0.2	2.8 \pm 0.3	2.5 \pm 0.3	2.7 \pm 0.3	2.6 \pm 0.2	1.7 \pm 0.0	2.2 \pm 0.3	1.7 \pm 0.3	1.7 \pm 0.4
Total extractable soil residues		94.4 \pm 0.1	92.5 \pm 0.4	91.6 \pm 0.3	87.0 \pm 1.2	85.1 \pm 1.2	76.5 \pm 0.8	75.1 \pm 0.6	75.7 \pm 1.2	77.0 \pm 0.9
Soda lime (presumed $^{14}\text{CO}_2$)		N/A ³	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0
Volatiles		N/A ³	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0	<0.1 \pm 0.0
Nonextractable soil residues		4.8 \pm 0.1	4.4 \pm 0.0	7.1 \pm 0.0	10.3 \pm 0.3	12.3 \pm 0.7	18.1 \pm 0.3	21.5 \pm 0.6	21.1 \pm 0.5	21.0 \pm 0.6
Total Recovery	Water ²	Not determined.								
	Soil ²	Not determined.								
	System	99.2 \pm 0.3	97.0 \pm 0.3	98.8 \pm 0.0	97.4 \pm 0.6	97.4 \pm 0.3	94.6 \pm 0.0	96.5 \pm 0.5	96.8 \pm 0.3	98.0 \pm 0.4

1. Data obtained from Table 5, p. 36 of the study report.

2. The water and soil layers were not analyzed separately.

3. N/A = Not analyzed.

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C. TRANSFORMATION OF PARENT COMPOUND: In the total system, [^{14}C]glufosinate decreased from an average 88.6% of the applied at 0 days posttreatment to 80.8% at 13 days, then varied between an average 70.3 to 72.7% at 29 through 125 days (Table 5, p. 36).

HALF-LIFE: Based on first order linear regression analysis (Excel 2000) and using data from individual samples, glufosinate ammonium dissipated with a calculated half-life of 415 days in the entire system (Appendix 7, p. 61; DER Attachment). Non-linear regression analysis (Excel 2000) of individual sample data yields a calculated dissipation half-life of 388 days in the entire system (p. 29, Figure 13, p. 53). However, non-linear analysis is an inferior descriptor of these data compared to linear regression. Also, calculated dissipation half-lives are of uncertain value because they are extrapolated well beyond the duration of the study.

Table 9: Calculated dissipation half-lives.¹

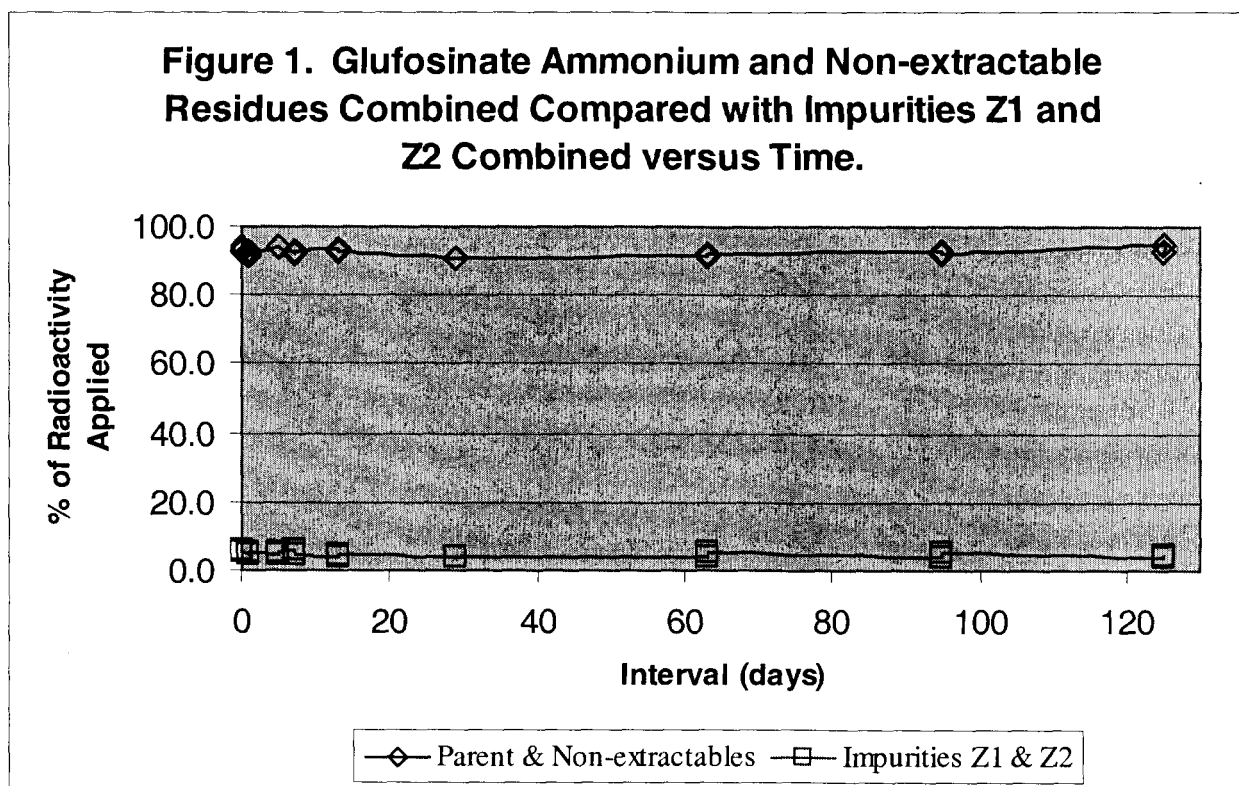
Medium	First-order Linear			Non-linear		
	Half-life (days)	Regression equation	r^2	Half-life (days)	Regression equation	r^2
Water	Could not be calculated.			Could not be calculated.		
Soil	Could not be calculated.			Could not be calculated.		
Total system	414.23	$y = -0.0017x + 4.4296$	0.6398	387.43	$y = 84.36x * e^{-0.001789t}$	0.6580

1. First order linear and non-linear half-life values were calculated using data obtained from Appendix 7, p. 61 of the study report (DER Attachment).

TRANSFORMATION PRODUCTS: No major transformation products were isolated (Table 5, p. 36). No minor transformation products were identified. Two minor extractable [^{14}C]residues identified as Z1 and Z2 were thought to be contaminants in the treatment solution, as they were present at #3.2% of the applied from 0 days posttreatment forward and did not change significantly during the study (DER Figure 1). Z1 and Z2 were associated with the ambient water extracts plus water layer; all [^{14}C]residues in the hot water plus acetonitrile:water extracts (1.47-6.30% of the applied) were identified as glufosinate ammonium (Appendix 6, p. 60).

NONEXTRACTABLE AND EXTRACTABLE RESIDUES: The concentration of extractable [^{14}C]residues in the system decreased from an average 94.4% of the applied at 0 days posttreatment to 75.1-77.0% at 63-125 days (Table 5, p. 36). The majority of extractable [^{14}C]residues were associated with the ambient water extracts plus water layer; extraction of the soil with hot water and acetonitrile:water removed an additional 1.47-6.30% of the applied (Appendix 6, p. 60). Nonextractable soil [^{14}C]residues increased to a maximum average of 21.0-21.5% of the applied at 63-125 days posttreatment (Table 5, p. 36).

VOLATILIZATION: At 125 days posttreatment, volatile [^{14}C]residues (CO_2 plus volatile organics) totaled <0.2% of the applied (Table 5, p. 36).



TRANSFORMATION PATHWAY: A transformation pathway was proposed by the study author (p. 30; Figure 14, p. 54). Glufosinate ammonium dissipates as a result of binding to the soil. The study author did not suggest whether glufosinate was transformed prior to binding.

Table 10: Chemical names for transformation products of glufosinate ammonium.

Applicant's code	CAS Number	Chemical Name	Chemical formula	Molecular weight	SMILES string
No transformation products were identified.					

D. SUPPLEMENTARY EXPERIMENT-RESULTS: No supplementary experiments were reported.

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III. STUDY DEFICIENCIES:

1. The aqueous phase decanted from centrifuged samples was not analyzed separately from the soil extracts (pp. 21-22). The three ambient water extractions of the soil and the water layer were combined and then analyzed by LSC and HPLC. Therefore, the partitioning ratio between the water and soil phases could not be calculated. Subdivision N and OECD guidelines indicate that identification and characterization of residues in both soil and aqueous phases should be performed.
2. The initial and final redox potentials in the soil layer were not reported. Redox potentials in the water layer ranged from -30 to -71 mV. Redox potentials in the range of -50 to +200 mV are considered moderately reducing and -200 to -50 mV reducing (Wolfe, *et al.*, 1990). OECD guidelines consider sediment and water to be anaerobic when the redox potential is lower than -100 mV. Therefore, anaerobicity was not achieved and maintained during the study.
3. A single field soil sample was collected for the sediment phase. The OPP Rejection Rate Analysis and OECD guidelines indicate that two aquatic sediments should be studied.
4. The water layer consisted of deionized water. For the aqueous phase, OECD guidelines advise the use of water associated with collected sediments sampled from the anaerobic zones of surface water bodies.
5. The concentration of unextracted [^{14}C]residues increased to a maximum of 21.5% of the applied radioactivity over time (Table 5, p. 36). Subdivision N guidelines specify that reasonable nondestructive attempts must be made to extract the test material and its transformation products from the soil, with a goal of reducing the concentration of non-extractable [^{14}C]residues to $\leq 10\%$ of the applied without formation of artifacts in the extract. The harshest extraction procedure used in this study was shaking with acetonitrile:water at room temperature. The study author did not demonstrate that a harsher extraction procedure would fail to extract additional identifiable residues. However, water extraction was sufficient to reduce non-extractable [^{14}C]residues to $\leq 11.6\%$ in a previously submitted anaerobic aquatic metabolism study (MRID 45215401).
6. The test soil used in the study was from Germany. The soil was fully characterized according to the USDA Soil Textural Classification system, but was not formally compared to a soil from the US (Table 1, p. 32).

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7. At the start of the study, the viability of the soil was measured as mg microbial carbon/kg soil (dry weight equivalent). At the termination of the study, the quantity of anaerobic bacteria in terms of colonies/mL was determined. The same procedures should be used to analyze soil viability at the start and termination of the experiment, so that the values can be compared and it can be determined if treatment affected the soil viability.
8. Levels of quantitation (LOQ) were not reported.
9. The nominal water:sediment ratio was 1.2:1 (m:m) or 1.4:1 (v:v). OECD guidelines advise the use of a water:sediment ratio between 3:1 and 4:1 (v:v).

IV. REVIEWER'S COMMENTS:

1. During the pre-incubation, the flasks were kept under a nitrogen atmosphere; they were purged with nitrogen prior to being sealed and the balloon was filled nitrogen (p. 17). Following treatment, the flasks and balloon were purged with argon. The study author did not explain the reason for the change in the gases that were used.
2. The nominal incubation temperature was reported as $20 \pm 1^{\circ}\text{C}$ (p. 12). The maximum temperature during the 125 days of incubation following treatment was 21.30°C , the mean temperature was 20.27°C (Appendix 3, p. 57).
3. The study author reported that the nominal application rate chosen for this study was based on the highest single field application rate of 1.5 kg a.i./ha, assuming a soil bulk density of 1.5 g/cm^3 and a soil depth of 5 cm (p. 14).
4. The study author reported the ambient soil extraction shaking time as 30 minutes in the text and as 45 minutes in the method flow chart (p. 21, Figure 6, p. 44).
5. The study was terminated at 125 days posttreatment, at which time 72.7% of the applied glufosinate ammonium remained free of degradation and unbound. Subdivision N guidelines specify that an anaerobic aquatic metabolism study should be conducted until the pattern of decline of the parent is clearly established. However, the study length is acceptable as the pattern of decline clearly indicated stability to degradation. In the study, glufosinate ammonium was 70.3 to 72.7% of the applied at 29 through 125 days.
6. The HPLC chromatogram of standards showed a good separation of peaks in the primary analysis (Figure 9, p. 49). The HPLC confirmatory method showed a good separation only on the parent compound. Retention times in both systems were not reported.

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EPA MRID Number 46258601

V. REFERENCES:

1. MRID 45215401. Stumpf, K. 1993. Hoe 039866-¹⁴C – Anaerobic Aquatic Metabolism of Glufosinate-ammonium in a Sandy Water Sediment System at Two Temperatures. Report ID CB91/092. Unpublished study performed and submitted by Hoechst Aktiengesellschaft, D-65926 Frankfurt am Main, Germany. 56 pp.
2. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 162-3, Anaerobic Aquatic Metabolism Studies. Office of Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/9-82-021.
3. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.
4. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010.
5. Wolfe, N., *et al.* 1990. Abiotic Transformations in Water, Sediments and Soil. *In* Pesticides in the Soil Environment, Soil Science Society of America, pp. 103-110.

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Attachment 1

Structures of Parent and Transformation Products

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

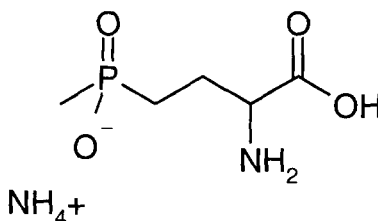
PMRA Submission Number {.....}

EPA MRID Number 46258601

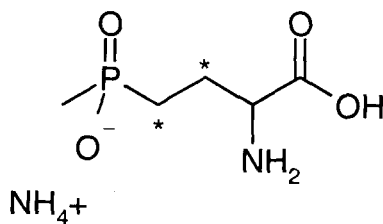
Parent Compound: Glufosinate ammonium [AE F039866; Hoe 039866]

IUPAC name: Ammonium DL-homoalanin-4-yl(methyl)-phosphinate.
CAS name: 2-Amino-4-(hydroxymethylphosphinyl)butanoic acid, ammonium salt.
CAS No: 77182-82-2.
SMILES string: CP(=O)(CCC(C(=O)O)N)[O-][N+].

Unlabeled



[3,4-¹⁴C]AE F039866



*Position of radiolabel.

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PMRA Submission Number {.....}

EPA MRID Number 46258601

Identified compounds

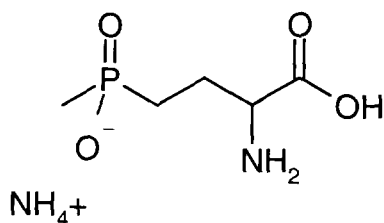
Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {

EPA MRID Number 46258601

Glufosinate ammonium [AE F039866; Hoe 039866]

IUPAC name: Ammonium DL-homoalanin-4-yl(methyl)-phosphinate.
CAS name: 2-Amino-4-(hydroxymethylphosphinyl)butanoic acid, ammonium salt.
CAS No: 77182-82-2.
SMILES string: CP(=O)(CCC(C(=O)O)N)[O-][N+].



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EPA MRID Number 46258601

Unidentified reference compounds

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

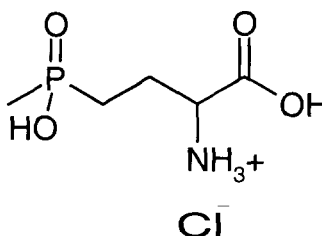
PMRA Submission Number {.....}

EPA MRID Number 46258601

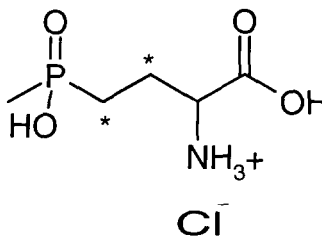
Glufosinate hydrochloride [AE F035125; Hoe 035125]

IUPAC name: DL-Homoalanin-4-yl(methyl)-phosphinate hydrochloride.
CAS name: Not reported.
CAS No: Not reported.
SMILES string: CP(=O)(CCC(C(=O)O)[N+])[Cl-]O.

Unlabeled



[3,4-¹⁴C]AE F035125



*Position of radiolabel.

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {.....}

EPA MRID Number 46258601

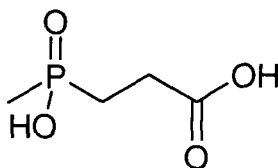
AE F061517

IUPAC name: 3-Methylphosphinico-propionic acid.

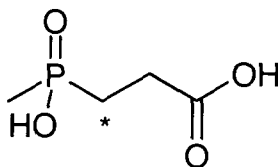
CAS name: Not reported.

CAS No: Not reported.

Unlabeled



[3-¹⁴C]AE F061517



*Position of radiolabel.

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {.....}

EPA MRID Number 46258601

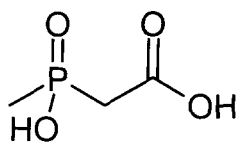
AE F064619

IUPAC name: 2-Methylphosphinico-acetic acid.

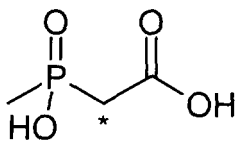
CAS name: Not reported.

CAS No: Not reported.

Unlabeled



[2-¹⁴C]AE F064619



*Position of radiolabel.

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {.....}

EPA MRID Number 46258601

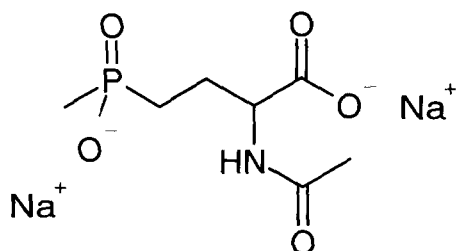
AE F099730

IUPAC name: Disodium L-2-acetamido-4-methylphosphinato-butyrate.

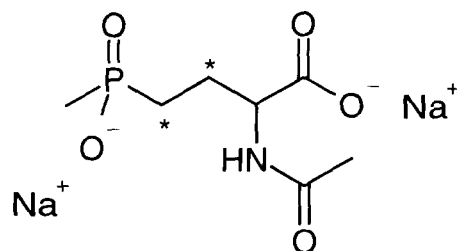
CAS name: Not reported.

CAS No: Not reported.

Unlabeled



[3,4-¹⁴C]AE F099730



*Position of radiolabel.

Data Evaluation Report on the Anaerobic Aquatic Metabolism of Glufosinate Ammonium

PMRA Submission Number {.....}

EPA MRID Number 46258601

Attachment 2

Excel Spreadsheets

Chemical Name Glufosinate ammonium
 PC Code 128850
 MRID 46258601
 Guideline No. 162-3

Material Balance

Interval (days)	Parent (% RA)	Z1 (% RA)	Z2 (% RA)	Non-extractable (% RA)	Recoveries (% RA)
0	89.0	2.6	2.9	5.0	99.5
0	88.2	2.6	3.4	4.6	98.8
1	88.3	2.1	2.5	4.3	97.2
1	86.7	2.4	3.0	4.5	96.6
5	86.7	2.3	2.2	7.2	98.4
5	86.9	2.3	2.7	7.1	99.0
7	82.5	2.8	3.0	9.7	98.0
7	81.4	2.0	2.4	11.0	96.8
13	79.7	1.8	2.4	13.7	97.6
13	81.8	1.7	2.8	10.9	97.2
29	73.2	2.3	1.7	17.6	94.8
29	71.8	2.2	1.7	18.7	94.4
63	71.4	2.5	1.8	20.3	96.0
63	69.2	2.8	2.5	22.7	97.2
95	70.4	2.7	1.4	22.0	96.5
95	71.6	3.2	2.1	20.2	97.1
125	72.1	2.6	1.3	22.3	98.3
125	73.2	2.6	2.1	19.7	97.6

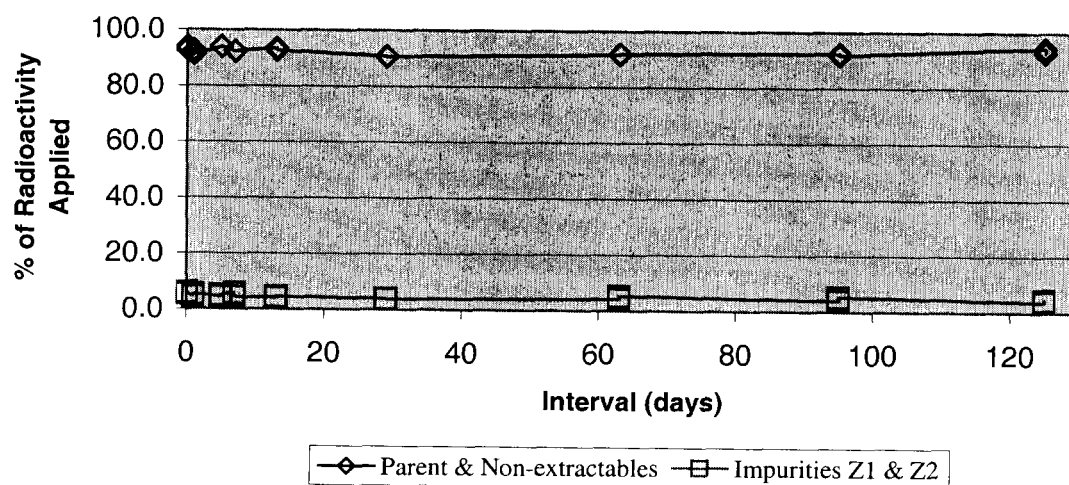
Data from Appendix 7, p. 61 of the study report.
 % RA means percent of radioactivity applied.

average 97.3
 SD 1.3

Chemical Name	Glufosinate ammonium
PC Code	128850
MRID	46258601
Guideline No.	162-3

Parent & Non-extractable (% RA)	Z1 & Z2 (% RA)
94.0	5.5
92.8	6.0
92.6	4.6
91.2	5.4
93.9	4.5
94.0	5.0
92.2	5.8
92.4	4.4
93.4	4.2
92.7	4.5
90.8	4.0
90.5	3.9
91.7	4.3
91.9	5.3
92.4	4.1
91.8	5.3
94.4	3.9
92.9	4.7

Figure 1. Glufosinate Ammonium and Non-extractable Residues Combined Compared with Impurities Z1 and Z2 Combined versus Time.



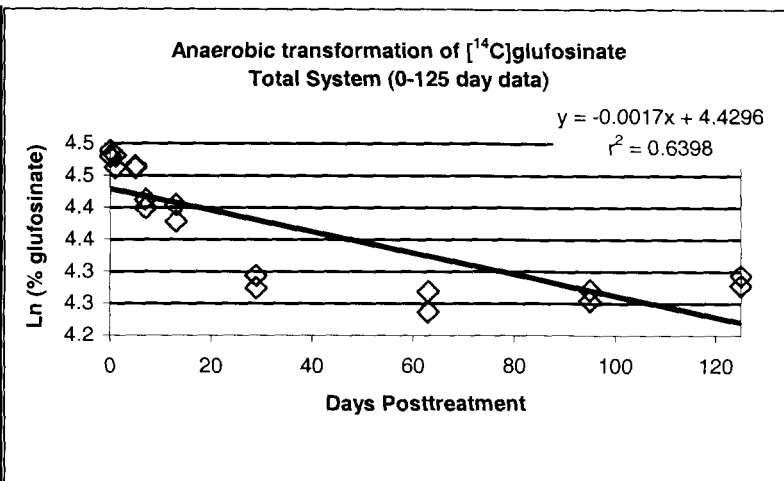
Chemical Name Glufosinate ammonium
 PC Code 128850
 MRID 46258601
 Guideline No. 162-3

Total system

Linear

Half-life (days) = 414.23

Interval (days)	Glufosinate (% RA)	Ln (Glufosinate) (% RA)
0	89.0	4.4886
0	88.2	4.4796
1	88.3	4.4807
1	86.7	4.4625
5	86.7	4.4625
5	86.9	4.4648
7	82.5	4.4128
7	81.4	4.3994
13	79.7	4.3783
13	81.8	4.4043
29	73.2	4.2932
29	71.8	4.2739
63	71.4	4.2683
63	69.2	4.2370
95	70.4	4.2542
95	71.6	4.2711
125	72.1	4.2781
125	73.2	4.2932



Data from Appendix 7, p. 61 of the study report.
 % RA means percent of radioactivity applied.

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.7998536
R Square	0.6397658
Adjusted R Squa	0.6172512
Standard Error	0.0578991
Observations	18

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	0.095257712	0.095258	28.41555	6.76E-05
Residual	16	0.053636944	0.003352		
Total	17	0.148894656			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	4.4296363	0.018033841	245.6291	4.79E-30	4.391406	4.467866	4.391406	4.467866
X Variable 1	-0.001673	0.000313908	-5.330624	6.76E-05	-0.00234	-0.00101	-0.002339	-0.00101

Chemical Name Glufosinate ammonium
 PC Code 128850
 MRID 46258601
 Guideline No. 162-3

Total system

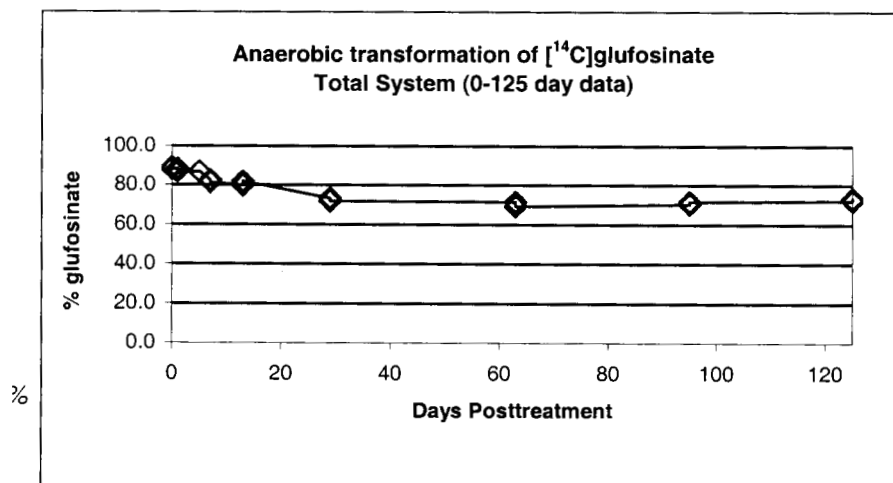
Non-linear

Half-life (days) = 387.43

C0	84.35759
k	0.001789
t 1/2	387.4346
SSE	317.1855
R^2	0.658008

Day	% RA	Est.	SE	Y^2
0	89.0	84.35759	21.55196	7921.0
0	88.2	84.35759	14.7641	7779.2
1	88.3	84.2068	16.75425	7796.9
1	86.7	84.2068	6.216022	7516.9
5	86.7	83.60635	9.570678	7516.9
5	86.9	83.60635	10.84814	7551.6
7	82.5	83.30773	0.652425	6806.3
7	81.4	83.30773	3.639428	6626.0
13	79.7	82.41825	7.38889	6352.1
13	81.8	82.41825	0.382235	6691.2
29	73.2	80.09247	47.5061	5358.2
29	71.8	80.09247	68.76501	5155.2
63	71.4	75.36579	15.72749	5098.0
63	69.2	75.36579	38.01697	4788.6
95	70.4	71.17227	0.596399	4956.2
95	71.6	71.17227	0.182954	5126.6
125	72.1	67.45301	21.59453	5198.4
125	73.2	67.45301	33.02791	5358.2

ANOVA					
Source	Df	SS	MS	F	p
Reg	1	610.2795	610.2795	30.78474	4.41E-05
Error	16	317.1855	19.82409		
Total	17	927.465			



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EPA MRID Number 46258601

Attachment 3

**Transformation Pathway Presented by Registrant
Illustration of Test System**

Figure 14 Proposed Degradation Pathway of Glufosinate In Soil Under Anaerobic Conditions

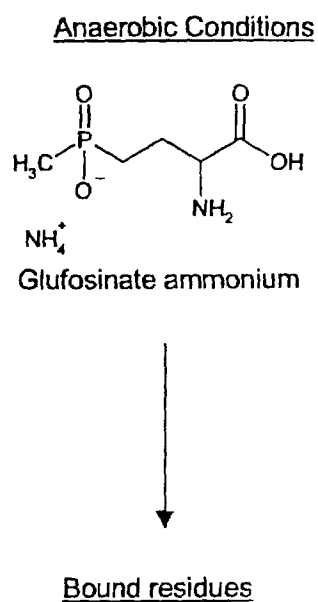


Figure 3 Test System Used for the Anaerobic Phase

Test system:

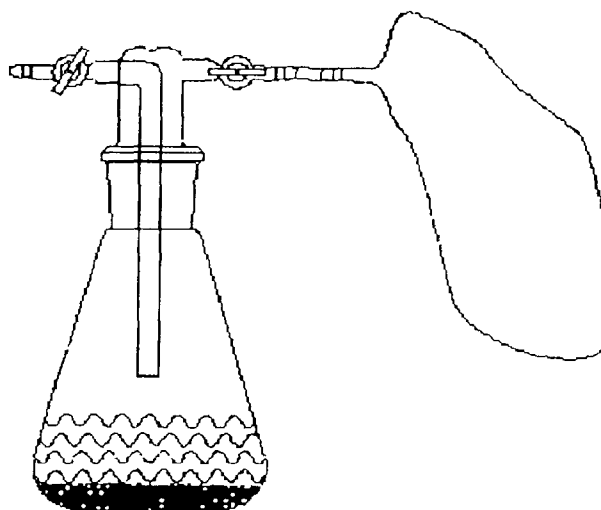
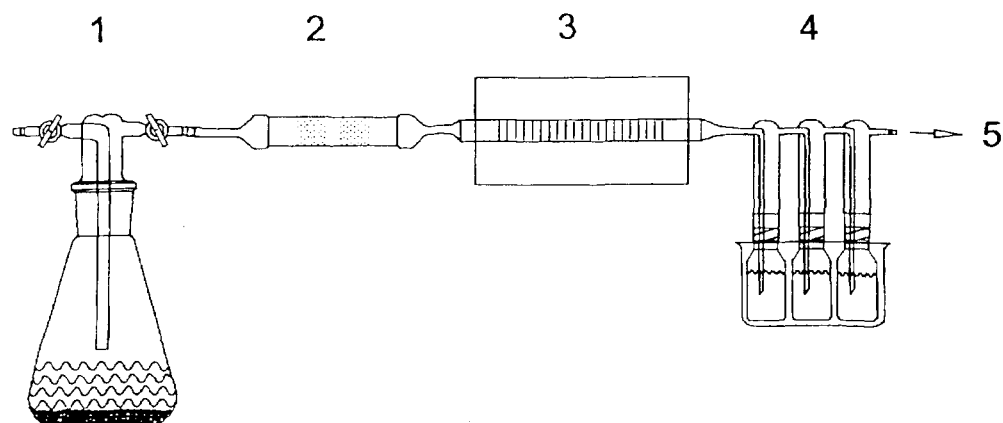


Figure 4 Analysis of Volatile Compounds Formed under Anaerobic Conditions

- 1 Incubation vessel
- 2 Trap for carbon dioxide, filled with 2 portions of about 5 g soda lime
- 3 Muffle furnace (about 950 °C), quartz glass tube filled with CuO
- 4 Vessels filled with scintillation cocktail (20 mL each) for carbon dioxide
- 5 Gas outlet (vacuum system)

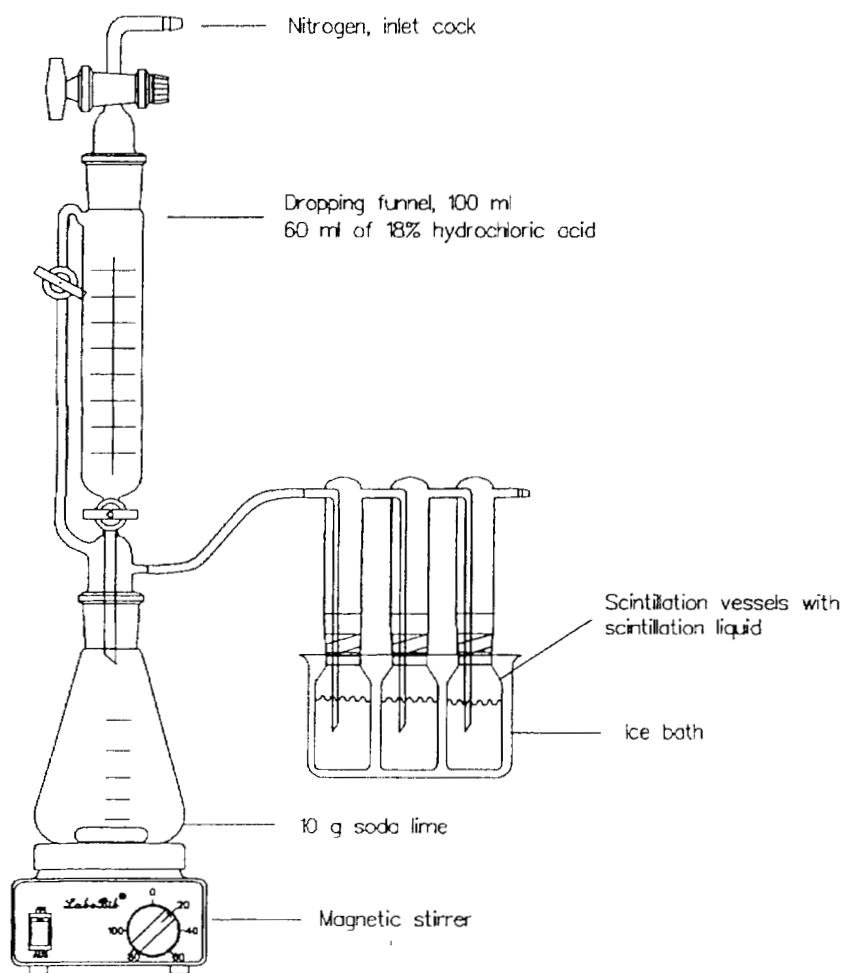
Figure 5 Device for Liberation of Bound CO₂ from Soda Lime

Figure 6 Procedure of Sample Analysis (Flow Chart)anaerobic Part